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Intrinsic bonding Defects in Non-crystalline (nc-) SiO_2 and GeO_2: Spectroscopic Detection of Differences between Vacancy Sites with and without O-atom occupancy

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1. Introduction to Defects

Electron spin resonance (ESR) studies on bulk-quenched silica (SiO_2) have distinguished between pre-existing, and X-ray/γ-ray induced defects [1]. Pre-existing defect densities increase exponentially with increasing quenching/annealing temperatures and are assigned to E' centers, singly occupied Si atom dangling bonds. Non-bonding O hole centers, NBOHC, increase linearly with the radiation dosage, are detected after X-rag/γ-ray irradiation. ESR features been addressed for local bonding as singlet to triplet state excitations.

2. Medium Range Order and Bonding

Medium range order (MRO), order beyond short range order bond-lengths & bond angles, and including four-atom dihedral angle correlations, was initially detected in nc-SiO_2 and GeO_2, by analysis of the spectral energy and width of the first sharp diffraction peak, FSDP [2]. MRO is present in 1 nm clusters comprised on 6 atom rings embedded in a disordered network of 5 and 7 member rings.

3. Pre-existing Defects in nc-SiO_2 and GeO_2

Pre-exiting defects have been detected by O K pre-edge X-ray absorption (XAS) 2nd derivative spectroscopy in remote plasma deposited (RPD) and thermally grown SiO_2 and GeO_2 thin films [3]. In this paper, they are addressed in the context of electronic spectroscopy and theory based on d-state ligand field splittings associated with molecular orbital theory des- criptions of valence band states. The model includes strongly correlated spin states of near-neighbor dangling bonds at vacated O-atom sites. Energy differences in dangling bonds at vacated O-atom sites. Energy differences between two electron singlet and triplet state ground states embedded in 1 mn locally-ordered clusters, and (ii) singlet and triplet excitations of vacated O-atom sites which give rise to states within the band gap detected by 2nd derivative XAS,

3. 2nd Derivative O-atom K pre-edge XAS Spectra

Figure 1 displays a 2nd derivative spectrum for RPD SiO_2 deposited at 300ºC and annealed in Ar at 950ºC for one minute. Qualitatively and quantitatively similar spectra have also been obtained with for RPD SiO_2 and GeO_2 [3]. These spectra also display (i) features associated singlet stabilized Si-Si and Ge-Ge bonds at vacated O-states, (ii) 4 singlet states, and 3 triplet terms with final state spin-orbit degeneracy removal (9-features), (iii) 3 additional singlet states which are negative ion states when occupied, and (iv) finally a band-edge singlet and 3 excition states at lower eV. In agreement with these assignments the intensity of Si-Si and Ge-Ge singlet bond defect features grows with increasing processing temperatures, and is greater in GeO_2, scaling with Si-Si and Ge-Ge bond energies

4. Local Dangling Bonds and Calculations

A vacated site is formed by removing the central O-atom. Figure 2 (lower part) indicates the dangling bonds resulting from a removal of an O-atom from a Si-O-Si bond angle of 140º, and Fig. 3 (upper), two dangling bonds in a linear geometry for calculations.

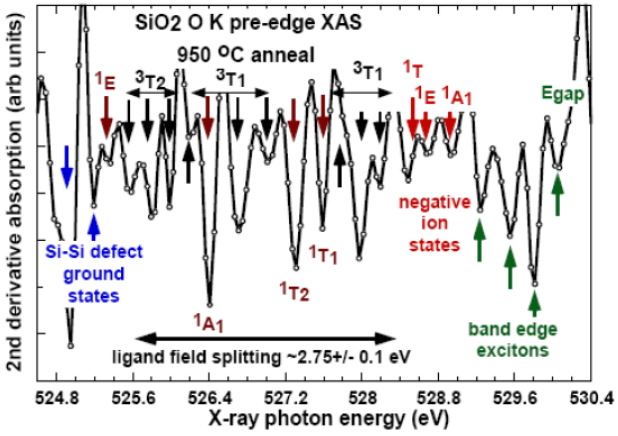

Fig. 1. O pre K-edge XAS for nc-SiO_2.

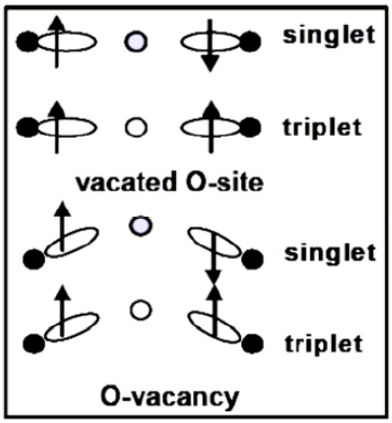

Fig. .2.. Local geometries for pair of dangling bond at vacated O-atom sites.

Total ground state energies including electronic states and bond geometries, and singlet and triplet excitation energies have been determined by ab initio calculations. Figure 3 displays singlet and triplet ground state energies as a Total

ground state energies including electronic states and bond geometries, and singlet and triplet excitation energies have been determined by ab initio calculations. Figure 3 displays singlet and triplet ground state energies as a function of the Si-Si inter-atomic distance. R, for removal of an O-atom. This distance is ~0.31 nm in an SiO_2 CRN network, and in crystalline SiO_2 as well. The energy difference between these 2 branches is an effective exchange energy, witth the decrease in the triplet state with increasing R displaying an ~$1/R^3$ dependence, and decreases in the singlet state energy with increasing R being driven by a decrease in the radial function overlap of the symmetric radical wave function dependence.

Figure 4 displays triplet energies for R=0.34 nm where the splitting between the two groups of states is more than 5 eV and much larger than the splitting between the singlet and triplet ground states show in Fig. 5 or R=0.49 nm. Figures 5(a) and (b) indicate respectively 3 strong triply degenerate triplet terms, and 5 strong singlet terms, three non-generate with Ag symmetry, and 2 doubly degenerate with Eg symmetry degeneracy giving 9 spectral features, and 7 singlet features. Final state effects remove the triplet degeneracy.

The spacings between the singlet and triplet features for this spacing are similar to those in Fig. 1 supporting the model for defect sites being vacated O-atom vacancies in which there has been a displacive transition to from ~ 0.3 to ~0.5 nm.

5. Summary

Pre-existing defects, identified in RPD nc-SiO_2 and GeO_2 thin films have been identified in O K pre-edge 2nd derivative spectra. Defects are embedded in 1 nm clusters defined by the FSDP. Ordering and singlet and triplet features is described by application of ab initio calculations, and for structural relaxations which give near degenerate singlet and triplet ground states.

This includes the variation of singlet and triplet excitations as a function of dangling bond separation.

References

[1] F.L. Galeener,J. Non-Cryst Solids 71 (1985) 373
[2] G. Lucovsky et al., Nanosci.e Lett. 5 (2010) 150.
[3] G. Lucovsky et al., Microelectronic Eng. 88 (2011) 1537.

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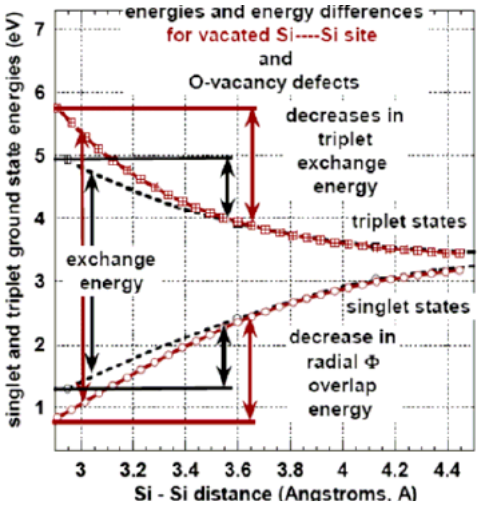
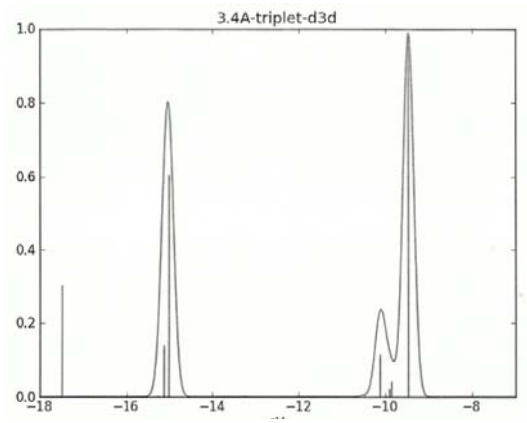
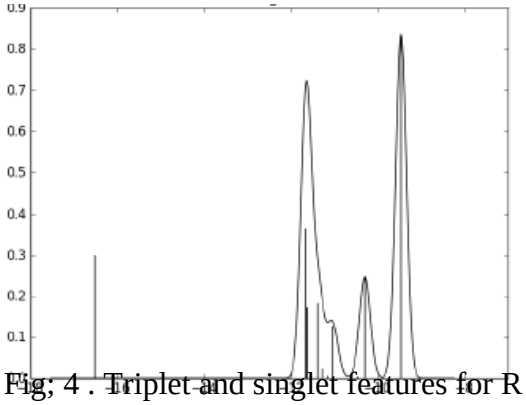


•Fig. 3. Singlet and triplet energies for thje bonding displayed in Fig.; 2.

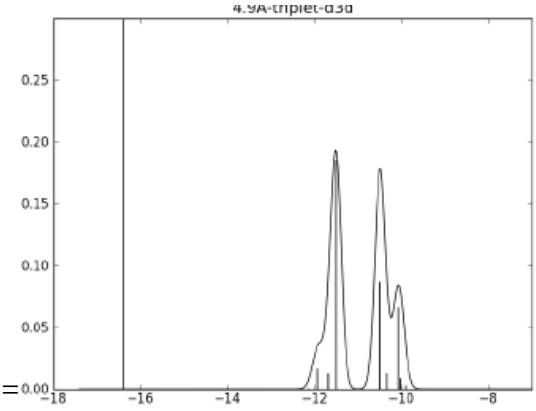


amplitude (arb units) vs. energy (eV)

Fig. 5. Singlet features for R = 0.34 nm.



Fig; 4 . Triplet and singlet features for R = 0.9 nm



amplitude (arb units) vs energy